

Exploratory Synthesis: Nitrides

Mark Bailey-Glenn Seaborg Distinguished Postdoc, J.F. Mitchell
Materials Science Division, Argonne National Laboratory

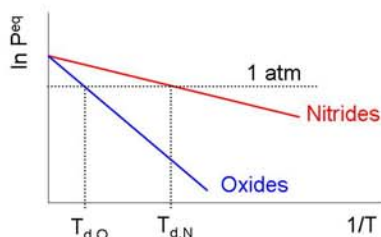
New Program in Materials Synthesis

- New materials present an opportunity for breakthrough advances in properties.
- Is oxygen important? i.e., the synthesis of complex nitrides will allow us to test the role of the anion in complex oxides.

Nitrides

Introduction

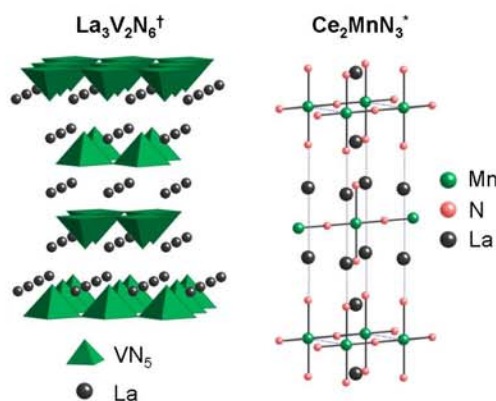
- The $\text{N}\equiv\text{N}$ is 500 kJ/mol stronger than the $\text{O}=\text{O}$ bond.
 - Most transition metal–nitrogen bonds are relatively weak.
- Therefore, $\Delta_f H^\circ$ is smaller for transition metal nitrides than for oxides: a given metal nitride will decompose at a lower temperature than its oxide:



This low decomposition temperature (T_d) enforces a low reaction temperature and prohibitively slow reaction kinetics!

Currently

Because of the thermodynamic and kinetic limitations, there are only ~15 known ternary $\text{R}_x\text{T}_y\text{N}_z$ (R = rare earth, T = Cr, Mn, V, Nb, Ta) compounds. Despite this scarcity, the structures are intriguing; e.g.,



Both compounds are metallic

Boron-Nitrides

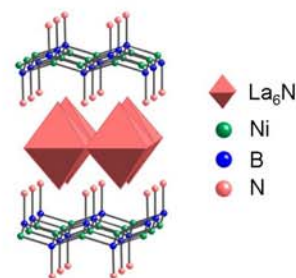
Introduction

- There are currently ~ 5 known $\text{A}_w\text{T}_x\text{B}_y\text{N}_z$ (A = electropositive element, T = transition metal) compounds:

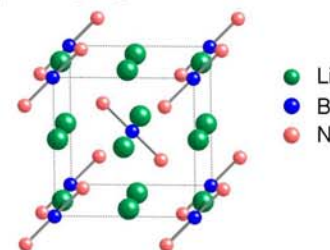


- All are layered structures.
- $\text{La}_3\text{Ni}_2\text{B}_2\text{N}_3$ is a superconductor with T_c of 13 K.

$\text{La}_3\text{Ni}_2\text{B}_2\text{N}_3$



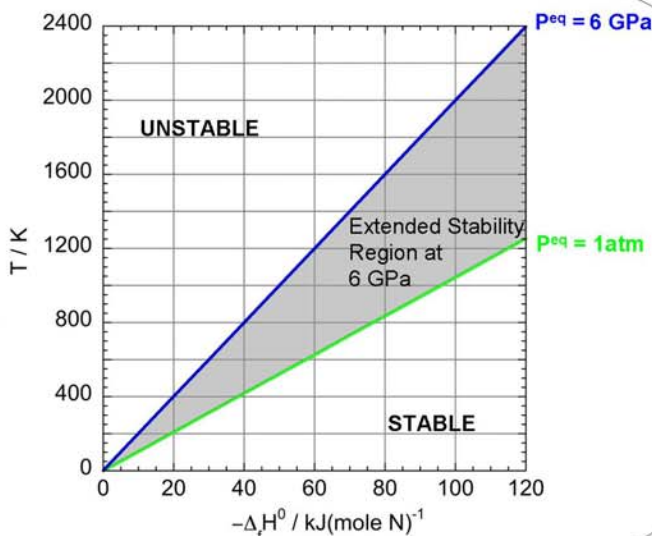
Li_3BN_2



- Li_3BN_2 melts congruently at 1189 K
- We intend to exploit Li_3BN_2 as a reactive flux for quaternary $\text{A}_w\text{T}_x\text{B}_y\text{N}_z$ compounds

High pressure synthesis is ideal

- The important factor is P^{eq} , the equilibrium N_2 partial pressure:
- We estimate that $|\Delta_f H^\circ|$ for $\text{R}_x\text{T}_y\text{N}_z$ is $\leq 70 \text{ kJ}(\text{mole N})^{-1}$
- Application of 6 GPa raises the stability regime by ~ 600 K, into regimes where appreciable diffusion and reactions can occur.
- We will use high pressure to synthesize $\text{La}_x\text{-(Mn, Ni, Co, Cu)}_y\text{-N}_z$.



Both systems have very few members; however, many of these compounds have interesting and compelling crystal structures.